

US EPA ARCHIVE DOCUMENT

This document was initially posted to this site on September 18, 2008. The current version of the document includes correction to two typographical errors to the formula on page 16. These typographical corrections did not cause any changes to the data or the summary information contained in the original document.

Availability of New Speciation Data for Some Areas that EPA Intends to Designate as Nonattainment

Neil Frank

Office of Air Quality Planning and Standards

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New speciation data are now available for PM_{2.5} design value monitoring sites in ten areas which EPA intends to designate nonattainment (NA) which previously have lacked speciation data. The ten areas are shown in the first table below. These states provided archived Federal Reference or Equivalent Method (FRM/FEM) Teflon filters to Desert Research Institute (DRI) in February-March of this year. EPA paid for the chemical analyses. Here is the link to the [Teflon filter speciation data file](#). Data description, analytical protocols and other background information are presented below. While EPA's preliminary judgment is that these new speciation data are helpful and generally confirm the designation proposals already made, EPA believes that they are not critical to the final determinations of NA area boundaries. The data and this explanation are being released via this document to facilitate State and public comment on the data and how they should be interpreted with respect to the designations process.

Background

NAAQS compliance or violation determinations are made only on the basis of FRM/FEM samplers. These PM_{2.5} samplers use a single Teflon filter to collect PM_{2.5}. In normal operation, the Teflon filter is weighed before and after sampling, producing a measurement of the mass of the collected PM_{2.5} and from that a value for the concentration of PM_{2.5} mass in the air. As described in EPA's Contributing Emission Score (CES)¹, knowledge of the species composition of ambient PM_{2.5} can be useful in understanding the types of emission sources that contribute to ambient PM_{2.5}. These relative contributions in turn can help in understanding the specific geographic areas where the significantly contributing source may be, the appropriate boundaries for NA areas, and eventually the design of emission control programs to reduce PM_{2.5} concentrations to reach attainment. The typical approach used to obtain this knowledge is to operate a separate multi-filter PM_{2.5} sampler, and subject the different filters to different types of chemical analysis aimed at quantifying different sets of chemical species. Because of the cost of doing so, such speciation samplers are not operated at all sites where FRM/FEM samplers operate. It has turned out that a number of FRM/FEM monitoring sites where there is no speciation sampler in operation are in violation of the 24-hour PM_{2.5} NAAQS, and EPA has identified areas around those monitors which EPA intends to be designated as NA. When speciation data have not been available at the design value location, EPA and the States have had to estimate PM_{2.5} composition using

¹ EPA's Contributing Emission Score (CES),
http://www.epa.gov/ttn/naqs/pm/docs/tsd_ces_methodology.pdf.

information from nearby monitors or other locations in the same geographical area. The latter is the speciation gap-filling approach presented in the CES.

While FRM/FEM Teflon filters normally are not chemically analyzed for PM_{2.5} species, it is possible to perform certain types of chemical analysis on them. In November 2007, EPA gave the State's areas and sites without routine speciation monitoring the opportunity to provide their archived FRM/FEM Teflon filters to EPA for laboratory analysis to estimate the PM_{2.5} chemical constituents that can be determined from a Teflon filter. These new data were intended to assist EPA and the States with the identification of boundaries for potential NA areas and to also assist with development of future control strategies if the areas are designated as NA.

A total of 20 areas in 12 States were identified for the investigation of chemical measurements from archived Teflon filters. These areas did not have chemical speciation samplers at the site which measured a violation of the 24-hr NAAQS using 2003-05 or 2004-06 data. For each selected site, a list of 10 to 15 high PM_{2.5} filter days was identified. The proposed FRM/FEM filter days had PM_{2.5} concentrations greater than the annual 95th percentile of measured values from 2004, 2005 or 2006. EPA offered to pay for the chemical analysis and promised to share the data with the States. EPA arranged for DRI to provide the chemical analyses. A list of requested filters and the planned chemical analysis protocol was provided to the EPA Regional Offices for communication with their States. Monitoring agencies operating thirteen such monitoring locations in 10 States chose to submit their FRM/FEM filters to EPA. The initial list, participating locations and their Air Quality System (AQS) site codes follow.

**20 DV sites without collocated Chemical Speciation Network data
proposed for new speciation analysis**

| EPA region | State | County | AQS Site | |
|-------------------|--------------|---------------|-----------------|---|
| 3 | PA | Lehigh | 420770004 | |
| 3 | PA | Mercer | 420850100 | |
| 4 | AL | Etowah | 010550010 | * |
| 4 | GA | Muscogee | 132150008 | |
| 5 | IN | Knox | 180830004 | |
| 5 | OH | Trumbull | 391550007 | |
| 5 | WI | Brown | 550090005 | |
| 5 | WI | Milwaukee | 550790043 | |
| 8 | MT | Ravalli | 300810007 | |
| 8 | UT | Cache | 490050004 | * |
| 8 | UT | Salt Lake | 490350003 | * |
| 8 | UT | Weber | 490570002 | * |
| 9 | AZ | Santa Cruz | 040230004 | |
| 9 | CA | Placer | 060610006 | |
| 9 | CA | Solano | 060950004 | * |
| 9 | CA | Sutter | 061010003 | |
| 10 | ID | Lemhi | 160590004 | * |
| 10 | ID | Shoshone | 160790017 | |
| 10 | OR | Klamath | 410350004 | |
| 10 | OR | Lane | 410392013 | * |

Monitoring agencies responsible for seven sites in 5 states either did not have archived filters or otherwise chose not to participate (indicated with *).

Archived FRM/FEM filters from four additional locations with collocated Chemical Speciation Network (CSN) sites were also solicited. These locations were selected to represent a variety of PM_{2.5} compositions and different geographic regions. The speciation analyses of these additional filters were primarily intended to permit comparison with the routine measurements from the CSN and to assist with the interpretation and use of the filter analyses at the other archived filter locations. Several locations with high nitrate concentrations were specifically included to examine the comparability of measurements from archived Teflon filters with routine CSN sampling. A list of filter days was also selected from days with measured PM_{2.5} greater than the annual 95th percentile of measured FRM PM_{2.5} during 2004, 2005 or 2006. Of the four proposed collocated FRM/CSN locations, the responsible monitoring agencies for three sites chose to participate. These locations are listed below. One agency chose not to participate.

| EPA Region | State | County | AQS Site Code |
|------------|-------|------------|---------------|
| 5 | OH | Lucas | 390950026 |
| 5 | WI | Milwaukee | 550790026 |
| 8 | UT | Salt Lake | 490353006 * |
| 9 | CA | Sacramento | 060670010 |

* Site did not submit filters to EPA for analysis

The State filters provided to EPA were stored under refrigeration for all or part of the period between the sampling day and shipment to the DRI laboratory. This information is provided below for completeness and potential assistance in understanding the new data.

| EPA region | State | County | City | AQS Site | Refrigeration |
|------------|-------|------------|---------------|-----------|---------------|
| 3 | PA | Lehigh | Allentown | 420770004 | 1 year |
| 3 | PA | Mercer | | 420850100 | 1 year |
| 4 | GA | Muscogee | Columbus | 132150008 | 2 years |
| 5 | IN | Knox | Vincennes | 180830004 | All |
| 5 | * OH | Lucas | Toledo | 390950026 | Not all |
| 5 | OH | Trumbull | Youngstown | 391550007 | All |
| 5 | WI | Brown | Green Bay | 550090005 | All |
| 5 | * WI | Milwaukee | Milwaukee | 550790043 | All |
| 8 | MT | Ravalli | Hamilton | 300810007 | 1 year |
| 9 | AZ | Santa Cruz | Nogales | 040230004 | All |
| 9 | CA | Placer | Roseville | 060610006 | All |
| 9 | * CA | Sacramento | Sacramento | 060670010 | All |
| 9 | CA | Sutter | Yolo City | 061010003 | All |
| 10 | ID | Shoshone | Placerville | 160790017 | All |
| 10 | OR | Klamath | Klamath Falls | 410350004 | 1 year |

* Collocated with CSN site

Analytical Procedures and Measurement Data

An analytical protocol is described in Attachment 1 which is the Scope of Work provided to DRI. A combination of X-ray Fluorescence (XRF) to provide elemental concentrations (e. g., calcium, iron, sulfur, etc) and Ion Chromatography (IC) to estimate ions (sulfate, nitrate, potassium, ammonium, etc.) is described. The measured elemental concentrations allow the estimation of crustal material, other metallic oxides and tracers for specific source emission influences. The ion measurements allow the estimation of sulfate and nitrate mass which can be major components of PM_{2.5} mass. No measurements of elemental carbon or organic carbon were made as part of this project, as these carbon species cannot be measured on Teflon filters using the thermal optical procedures that are standard in the CSN. However, carbonaceous mass can be fairly well estimated by material balance using estimated sulfate, nitrate and crustal mass with the SANDWICH method². For the three study sites with collocated CSN and FRM measurements, the CSN data presented below have been adjusted by SANDWICH methods to represent the composition that would have been measured by the FRM. These adjusted CSN data are available at www.epa.gov/airexplorer/. These adjustments to the CSN data are the same as made as part of EPA's Contributing Emissions Score method for sites with CSN data.

To allow for the possible loss of semi-volatile nitrate with XRF analysis, only half of the filters collected during the cooler months of October – April were subjected to XRF. This analytical procedure subjects the filters to a vacuum and high temperature, under which conditions nitrate can potentially evaporate. To explore the effect of XRF on nitrates, a subset of filters at the three comparison sites were subjected to XRF before IC.³ These data could be useful to guide future study of archived Teflon filters.

Elemental carbon (EC) is nearly always only a small constituent of PM_{2.5} mass but can suggest potential influencing sources of the estimated total carbon component. To provide an indicator of elemental or black carbon, all of the Teflon filters were analyzed for filter transmittance using a densitometer.⁴ This estimate of the darkness of the filter has previously been shown to be highly correlated with EC produced by thermal optical methods at a collocated speciation monitor⁵. Such findings are also evident in this study from the comparison of darkness of the FRM/FEM filters from the three sites with CSN data and the actual EC measurement from the CSN sampler filter. However, no attempt has been made so far to use this correlation to estimate the amounts of EC on the Teflon filters at the 13 sites without CSN data.

In the [Teflon filter speciation data file](#), separate worksheets contain the data and definitions of data column headings and definitions of occasional data qualifiers. The PM_{2.5} mass concentration is also provided, as reported by the State. All of the chemical

² Frank, N. H., "Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities," *J. Air & Waste Manage. Assoc.* **2006**, 56, 500-511.

³ DRI uses a PanAnalytical unit for XRF. The level of XRF heating may be relevant in interpreting the nitrate results following XRF.

⁴ <http://www.densitometers.net/transmission.asp>

⁵ Watson J. G., and J. C. Chow, Comparison and evaluation of in situ and filter carbon measurements at the Fresno Supersite, *J. Geophys. Res.*, 107 (D21), 8341, doi :10.1029/2001JD000573, 2002.

data are in micrograms per cubic meter using the nominal sampler volume of 24 cubic meters and an assumed volume uncertainty of 2%. The mass DRI measured on the filters before and after XRF analysis is reported in micrograms per filter. This tab also includes some filters weighed again which did not get XRF. Worksheets are included for all the XRF data and, merely for convenience, also separately for a subset of 25 elements with higher detection limits and generally higher concentrations.

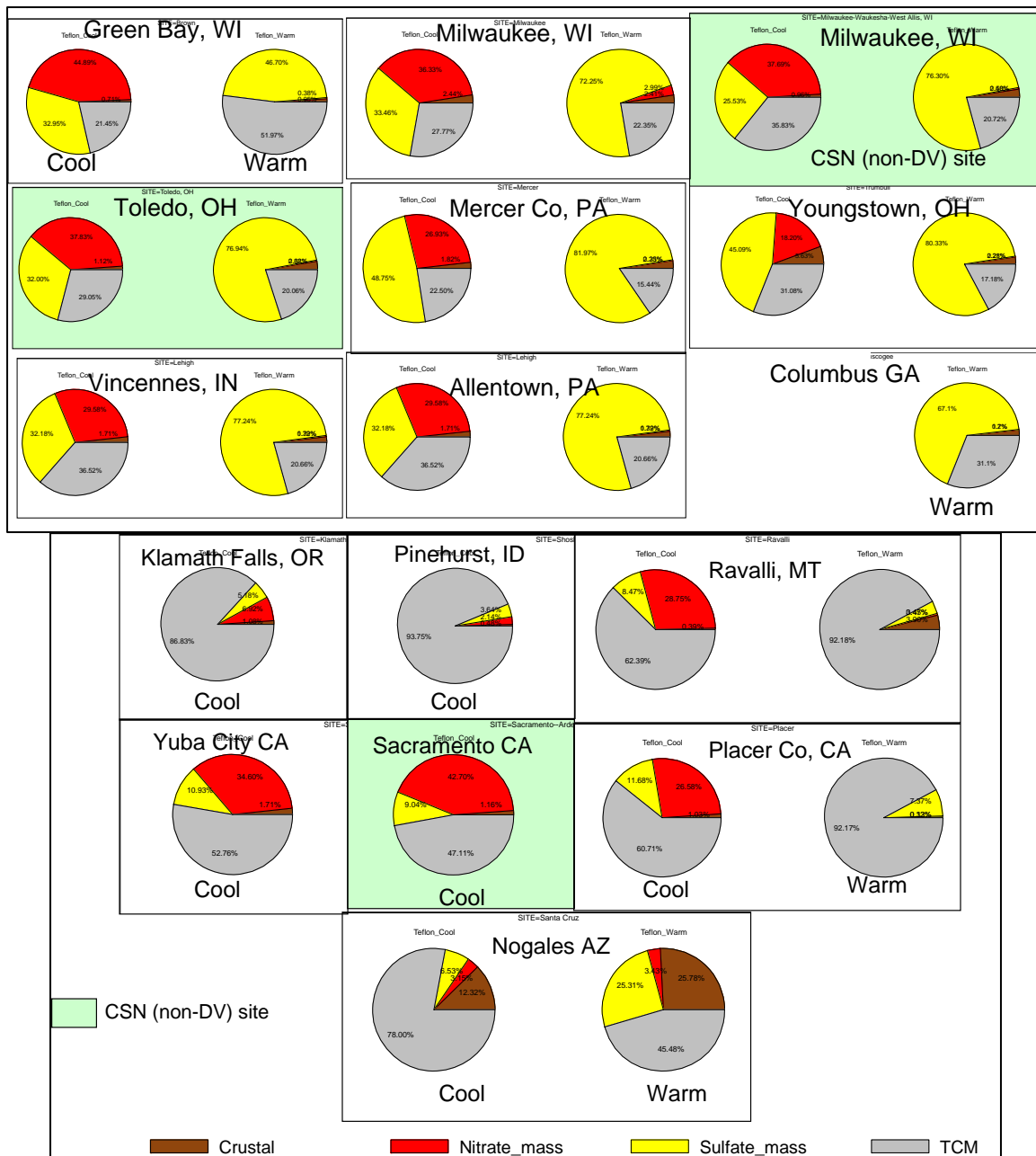
Summary of New Findings.

A summary of the estimated major components of PM_{2.5} is provided below. Based on the filter selection criteria, these averages are representative of the top 5 percent of measured PM_{2.5}. The data in ug/m³ are organized by season: May-September (warm) and October-April (cool). The total number of analyzed filters and the number to which were subjected to IC and/or XRF is indicated. Sacramento, Toledo and Milwaukee site 550790026 are the sites that are collocated with CSN monitors. Some of those filters received IC and XRF.

| State | County | AQS Site | season | no. filters | no. IC | no. XRF | FRM mass | Sulfate | Nitrate | TCM | Crustal |
|-------|------------|-----------|--------|----------------|-----------|------------|-------------|---------|---------|------|---------|
| AZ | Santa Cruz | 040230004 | Cool | 9 | 4 | 5 | 41.4 | 1.2 | 1.3 | 33.0 | 4.2 |
| AZ | Santa Cruz | | Warm | 1 | 1 | 1 | 48.5 | 12.3 | 1.7 | 22.1 | 12.5 |
| CA | Placer | 060610006 | Cool | 9 | 4 | 5 | 33.8 | 1.8 | 9.4 | 21.3 | 0.3 |
| CA | Placer | | Warm | 1 | 1 | 1 | 47.0 | 3.5 | 0.1 | 43.3 | 0.2 |
| CA | Sacramento | 060670010 | Cool | 12 | 12 | 6 | 39.2 | 3.5 | 16.8 | 18.2 | 0.9 |
| CA | Sutter | 061010003 | Cool | 14 | 7 | 7 | 33.4 | 1.9 | 12.3 | 17.9 | 0.6 |
| GA | Muscogee | 132150008 | Cool | 1 | 0 | 1 | 29.3 | 6.0 | | | 1.2 |
| GA | Muscogee | | Warm | 7 | 7 | 7 | 33.8 | 22.7 | 0.1 | 10.5 | 0.6 |
| ID | Shoshone | 160790017 | Cool | 16 | 8 | 8 | 38.5 | 0.7 | 0.8 | 35.4 | 0.2 |
| IN | Knox | 180830004 | Cool | 4 | 2 | 2 | 32.0 | 10.1 | 9.4 | 6.7 | 0.3 |
| IN | Knox | | Warm | 12 | 12 | 12 | 37.7 | 31.9 | 0.1 | 5.1 | 0.6 |
| MT | Ravalli | 300810007 | Cool | 13 | 6 | 7 | 39.3 | 1.6 | 11.8 | 24.9 | 0.1 |
| MT | Ravalli | | Warm | 1 | 1 | 1 | 22.5 | 0.8 | 0.1 | 20.7 | 0.9 |
| OH | Lucas | 390950026 | Cool | 5 | 5 | 3 | 32.8 | 10.4 | 12.3 | 9.5 | 0.6 |
| OH | Lucas | | Warm | 6 | 6 | 6 | 36.0 | 27.7 | 0.1 | 7.2 | 0.9 |
| OH | Trumbull | 391550007 | Cool | 6 | 3 | 3 | 34.9 | 9.4 | 7.6 | 12.9 | 2.3 |
| OH | Trumbull | | Warm | 10 | 10 | 10 | 33.7 | 27.1 | 0.1 | 5.8 | 0.8 |
| OR | Klamath | 410350004 | Cool | 12 | 6 | 6 | 42.1 | 1.1 | 3.0 | 36.8 | 0.5 |
| PA | Lehigh | 420770004 | Cool | 10 | 6 | 4 | 35.1 | 7.4 | 11.3 | 13.9 | 1.0 |
| PA | Lehigh | | Warm | 12 | 12 | 12 | 36.5 | 28.2 | 0.1 | 7.5 | 0.6 |
| PA | Mercer | 420850100 | Cool | 8 | 4 | 4 | 37.7 | 12.2 | 13.5 | 11.3 | 0.9 |
| PA | Mercer | | Warm | 12 | 12 | 12 | 34.1 | 28.0 | 0.1 | 5.3 | 0.8 |
| WI | Brown | 550090005 | Cool | 11 | 6 | 5 | 32.4 | 6.3 | 15.8 | 7.5 | 0.3 |
| WI | Brown | | Warm | 2 | 2 | 2 | 49.6 | 23.2 | 0.2 | 25.8 | 0.5 |
| WI | Milwaukee | 550790043 | Cool | 9 | 4 | 5 | 39.2 | 6.8 | 16.6 | 12.7 | 0.9 |
| WI | Milwaukee | | Warm | 7 | 7 | 7 | 36.8 | 26.6 | 1.1 | 8.2 | 0.9 |
| WI | Milwaukee | 550790026 | Cool | 7 | 7 | 4 | 38.1 | 9.7 | 14.3 | 13.6 | 0.6 |
| WI | Milwaukee | | Warm | 5 | 5 | 5 | 36.3 | 27.7 | 0.2 | 7.5 | 0.9 |

Pie chart representations are provided in Figure 1. The sulfate and nitrate mass derived from the Teflon filter measurements were adjusted for particle bound water using an equation which approximates the Aerosol Inorganic Model (AIM) procedure used by SANDWICH. This polynomial equation and associated computational steps are presented in Attachment 2. For the pie charts presented here, the approximately 0.5 ug/m³ mass associated with the FRM filter blank is included in the denominator for purposes of computing pie chart percentages.

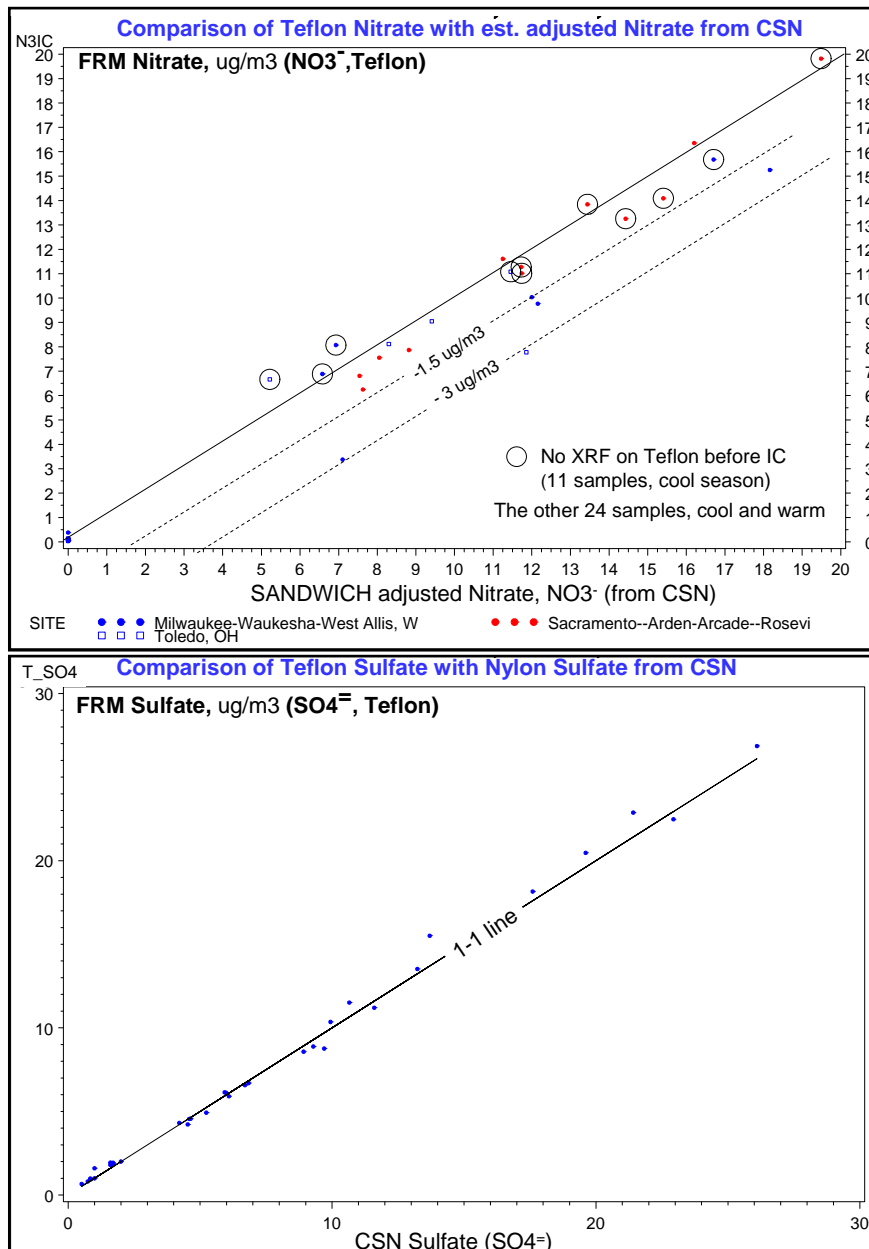
Figure 1. Pie chart representations of the chemical composition of high day PM_{2.5} derived from archived Teflon filter measurements (subset of days > 95th percentile of measured PM_{2.5}).



Comparisons with Collocated CSN data

To help interpret the new data, comparison data for the three collocated FRM-CSN sites are provided below. First are scatter diagrams of sulfate ion and nitrate ion (with and without XRF), presented in Figure 2. The new measurements from the archived Teflon filters are shown on the vertical axis and the measurements from the routine CSN monitoring using a nylon filter are on the horizontal axis. The solid diagonal line is the 1:1 line.

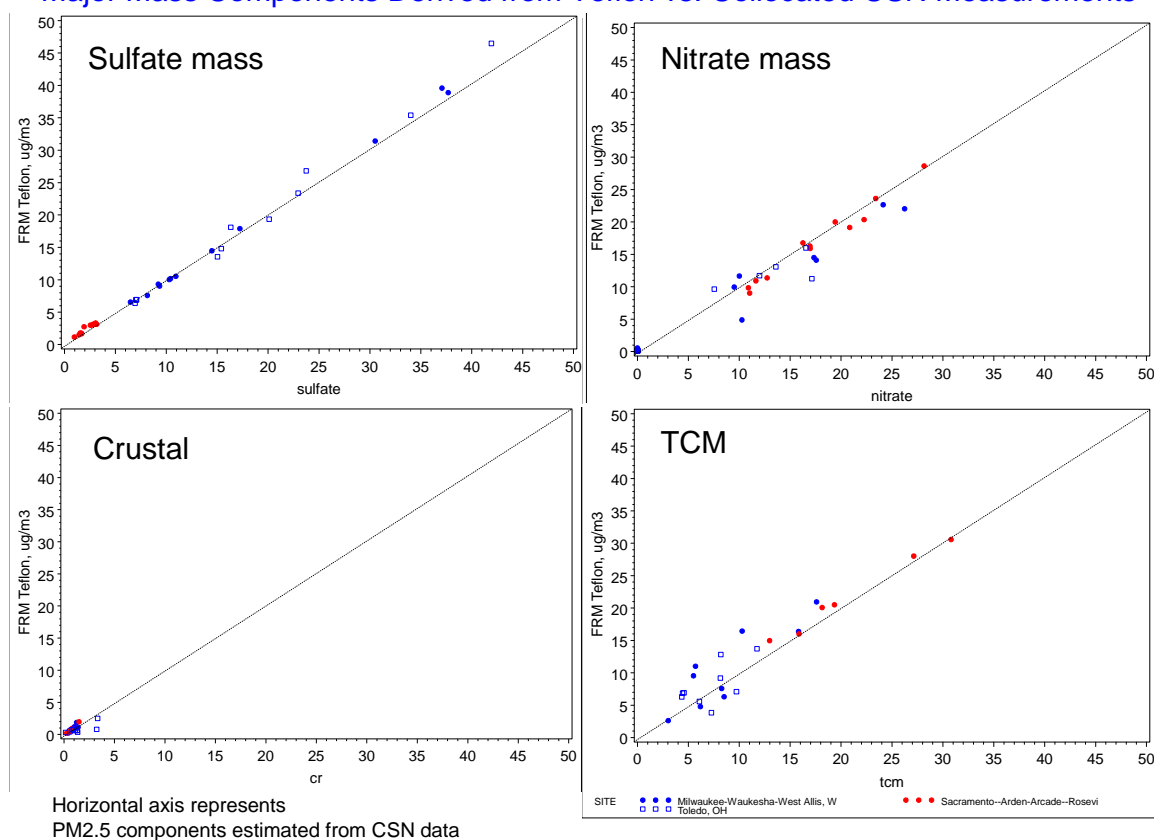
Figure 2. Comparison of Teflon Nitrate and Teflon Sulfate with CSN ion measurements.



Next, a comparison of estimated sulfate, nitrate, crustal and total carbonaceous mass using the SANDWICH adjustments is presented in Figure 3. Note that the sulfate mass and nitrate mass panes in Figure 3 are based on the same data as shown in Figure 2, but are presented as sulfate and nitrate mass which include associated ammonium and particle bound water. The axes are also different than those in Figure 2 to permit the full range of the data to be visible. Also note that all four panes in Figure 3 use the same axes ranges (0 to 50 ug/m³), making it easier to put the magnitude of the four major PM_{2.5} mass component concentrations into relative perspective. The points under the one-to-one line for nitrate mass correspond to those measurements made after XRF.

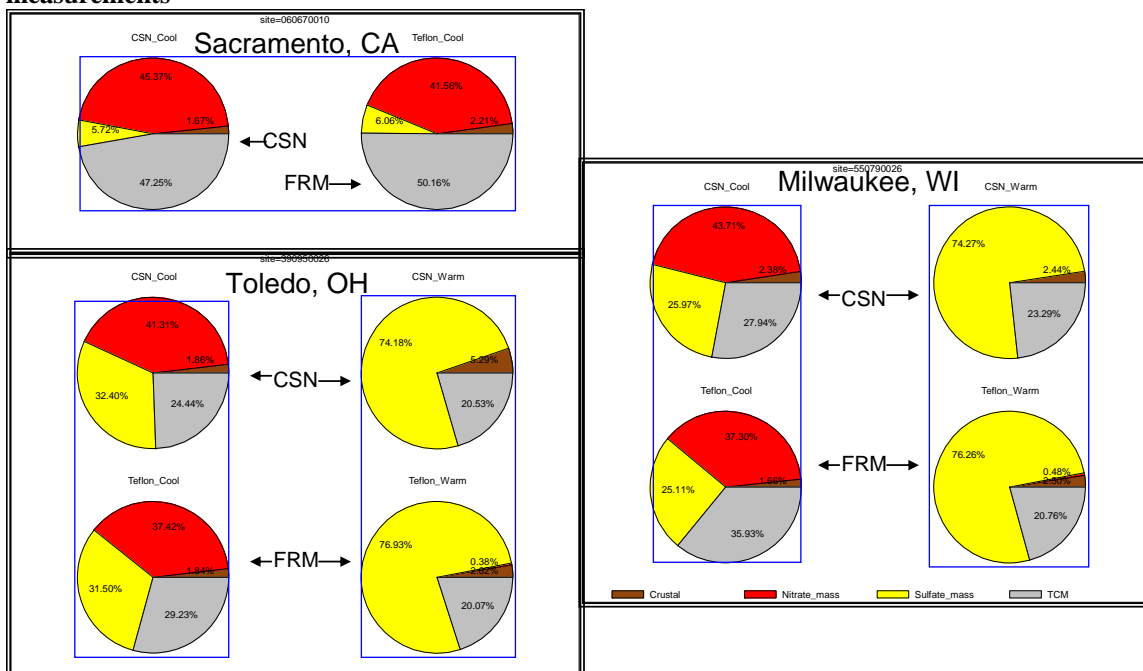
Figure 3. Major PM_{2.5} Mass components derived from FRM/FEM Teflon vs. collocated CSN measurements

Major Mass Components Derived from Teflon vs. Collocated CSN Measurements



Finally, pie chart comparisons of estimated PM_{2.5} composition using the new Teflon filter measurements and that using the routine CSN data are shown in Figure 4. Separate pies are shown for the cool and warm season data. The FRM derived nitrates in the cool season are lower in part because some of these filters received XRF prior to their ion analyses. This was also shown in Figure 3.

Figure 4. Pie chart comparisons of PM_{2.5} composition derived from FRM/FEM Teflon and CSN measurements



Attachment 1: Chemical Analysis of 412 Archived PM_{2.5} FRM Filters from State or Local agencies (Scope of Work with Desert Research Institute)

Project Purpose

The purpose of this project is to provide the Environmental Protection Agency (EPA) and State/local air officials information, otherwise unavailable, on the composition (or speciation) of ambient PM_{2.5} from monitoring sites and sampling days which are of relevance to attainment/nonattainment designations under the revised 24-hour PM_{2.5} NAAQS and/or to the development of emission source control strategies for areas which may be designated nonattainment. The data obtained from this project will be used to fill the current composition data gap for those areas without speciation monitors or without speciation at the site with the highest PM_{2.5} FRM mass.

Knowing the composition of PM_{2.5} is relevant to designations because it can provide insights into the source types that have contributed to PM_{2.5} NAAQS violations, which in turn can provide insights into what geographic areas should be included in a nonattainment area on the basis of their contribution to the monitored violations. Similarly, knowing the composition of PM_{2.5} is relevant to the development of emission source control strategies for a designated nonattainment area because it can help identify the source types most usefully controlled and, indirectly, the geographic areas where controls should be applied.

Approach

Teflon PM_{2.5} gravimetric mass filters from State/local monitoring sites without co-located speciation samplers, which have been kept refrigerated under State/local custody since the gravimetry, will be analyzed for ions, elements, and light absorption. Elemental carbon will be estimated based on the light absorption measurements. Organic carbon will be estimated, or at least bounded, through mass closure.

A 48-filter method confirmation phase of this project will test the comparability of the results from analyses under this project with data from Chemical Speciation Network (CSN) sites, using filters from FRM sites that had collocated CSN sampling. (Adjustments will be made to CSN data using the SANDWICH technique by EPA to correct for known differences between FRM samplers/filters and CSN sampler/filters with respect to positive and negative sampling artifacts. See http://www.epa.gov/cgi-bin/htmSQL/mxplorer/query_spe.hsrl and Frank, N. H., "Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities," *J. Air & Waste Manage. Assoc.* **2006**, *56*, 500-511. These collocated filters will be selected from days and sites which are appropriate for this comparability testing based on their season, geographic locale, and measured PM_{2.5} mass, but which are not of high interest for designations or control strategy development. This phase will check whether the storage and handling of the Teflon filters has altered their mass or composition. It will also allow the development, along with other available data, of a relationship between light absorption and elemental (black) carbon filter loading.

Following verification of the methods to be used, approximately 394 field-collected filters obtained from state/local archives will be analyzed. Most of these PM_{2.5} Teflon filters have been selected from high PM_{2.5} concentration days primarily from NAAQS violating sites without co-located Chemical Speciation Network (CSN) or IMPROVE data.

Background

EPA's revised National Ambient Air Quality Standards for PM_{2.5} became effective on December 18, 2006. EPA retained the annual PM_{2.5} standards of 15 µg/m³ and revised the 24-hour PM_{2.5} standards, changing them from 65 µg/m³ to 35 µg/m³.

The designation process for the revised 24-hour PM_{2.5} standards is the next step toward developing and implementing emission control programs for attaining and maintaining the revised standards. On June 8, 2007, EPA issued guidance for states and tribes to use in identifying areas that meet or do not meet EPA's recently revised national air quality standards for PM_{2.5} concentrations over a 24-hour period.

(http://www.epa.gov/ttn/oarpg/t1/memoranda/meyers_memo060807.pdf) States and tribes are required to submit their initial recommendations to EPA by December 18, 2007. States and tribes will make their recommendations using the data for the years 2004 – 2006. EPA will review and consider those recommendations, and will notify states and tribes of any modifications EPA wishes to make to state or tribal recommendations. If new air quality data are available (e.g., PM_{2.5} mass for the year 2007 or speciation data for recent years), EPA will take these data into consideration when making final designations. The Clean Air Act requires EPA to complete the designation process within two years of the effective date of the standard unless the Administrator finds that additional information is needed to make these decisions. In such a case, EPA may take up to an additional year to make the designations, i.e., no later than three years after the effective date of the standard.

When determining boundaries in urban areas for the annual PM_{2.5} standards several years ago, EPA applied a presumption that the boundaries for urban nonattainment areas should be based on metropolitan area boundaries as defined by the U.S. Office of Management and Budget. For the PM_{2.5} 24-hour standards, EPA is establishing no such presumption. In developing boundary recommendations for nonattainment areas for the 24-hour PM_{2.5} standards, the June 8, 2007 guidance encourages states and tribes to evaluate each area on a case-by-case basis. For each monitor or group of monitors that indicate violations of the standard, nonattainment area boundaries should cover a sufficiently large area to include both the area that violates the standard and the areas that contribute to the violations.

While many of the areas that experienced violations of the new 24-hour PM_{2.5} NAAQS in recent years have been operating PM_{2.5} speciation monitors that can provide composition information, of either the CSN or IMPROVE type or both, some of the areas lack such monitoring. EPA has identified 460 site-days from the latter areas that are of interest for this project. These 460 filters were collected in 20 counties in 12 states from Regions 3, 4, 5, 8, 9 and 10. EPA will contact monitoring officials in these areas for the purpose of obtaining access to archived filters from these site-days, and also access to associated data need for this project such as integrated sampler flow and filter tare and final weights. EPA will provide the contractor with a list of the target site-days and the contact information for the state/local officials who have agreed to coordinate the transfer of the filters and required associated data from the original field sampling operation.

The participating States will provide a "field data" file that contains sample IDs, method code, sampling site code (includes state code, county code, and site ID) and address, sampling date and time, reported PM_{2.5} mass concentration, flow rate, flags, method code, and pollutant occurrence code (POC). EPA will also provide the exposed area (e.g. DRI uses 11.78 cm² for Texas Teflon-membrane filter normalization). A minimum of three laboratory blanks (for pre-babs and for XRF analysis) will also be provided, preferably from the same batch for each State. For gravimetric analysis, the contractor will need to have the initial and post-weight comparison in mg/sample with corresponding IDs of each sample.

Statement of Work

From the selected filters, selected elemental contents will be obtained from: (1) more than half the filters using XRF; (2) more than half using ion chromatography ; (3) all filters using visible light transmission by densitometry. Note that some filters will get XRF analysis only; some filters will get IC analysis only; and the remaining filters will get both XRF and IC as described in the tasks below. The States will provide flow rates to permit the new Teflon filter chemical speciation measurements to be converted into ambient concentration values. Results of the analysis will be provided to the EPA and the States/Tribes by entry into the AQS system.

Task 1 – Prepare of Work Plan

The contractor shall prepare a simple work plan of sufficient detail to demonstrate understanding of and adequate plan for performing the remaining listed tasks in this Statement of Work, including any steps that are required for successful achievement of the stated objective but which are not stated explicitly in the descriptions of the remaining tasks

The work plan shall include copies of the Standard Operating Procedures to be used for the ions, elements, and light absorption measurements.

The work plan shall include copies of any associated data sheets or filter custody tracking form proposed to be used.

The work plan shall include an estimated schedule for completion of all tasks. The plan may assume that the analyses required in Tasks 3 and 4 will be done in “batch mode” once all filters for each task have arrived.

The Work Plan shall have adequate content to serve, along with other contractor documents referenced in the Work Plan, as a Quality Assurance Project Plan (QAPP) meeting the substance required of Tier X QAPPS under OAQPS’s tiered approach for such plans (add citation).

Task 2 – Analyze Five Blank Filters

The contractor shall analyze a minimum of 3 standard blank Teflon filters to be provided by EPA for light absorption, elements, and ions to determine filter background levels for comparison to later field samples. This is also needed to properly interpret and make adjustments if any for the XRF and IC analyses. Also, if there is sufficient uniformity in light absorption for these blanks then an optical measurement using a photographer’s densitometer (B_{abs} measurement) can be related to the EC filter loading via an absorption efficiency.

For XRF, the suite of 24 elements listed in Table 1 shall be analyzed.

The suite of three anions to be measured consists of chloride, nitrate and sulfate.

The order of analysis of these blank filters will be light absorption, XRF, and ions.

Deliverable: A written data report and recommendation as to whether the uniformity in the measurements on these blank filters is sufficient for the project to proceed to the remaining tasks. The report can be in the form of a memo to EPA.

Task 3 – Obtain and Analyze 48 State/local Field-Collected Filters to Test the Validity of Methods, and Prepare Report

The contractor shall contact the identified state/local monitoring officials to arrange for appropriate packaging and pre-paid shipping of the 48 filters identified in attachment 1.1 as targets for this Task (not included in this document).

For these 48 field samples, the following filter chemical analyses will be performed: 12 with XRF and IC, 18 with XRF only, and 18 with IC only. Attachment 1.1 identifies which filters will have which chemical analyses. All 48 filters will have light absorption measurements made. The order of multiple analyses will be the same as in Task 2.

To evaluate the impact of filter storage and filter transit on these 48 Teflon filters, gravimetry will be performed to compare with State derived FRM mass concentration. To judge the impact of XRF analysis on PM_{2.5} mass and potential loss of its volatile components, gravimetry will be performed a second time, after the XRF analyses. This information will be used in assessing the quality and interpretation of Task 3 chemical analyses.

The contractor shall calculate element and ion ambient concentrations for these filters, using the integrated sample flow obtained from the state/local monitoring officials.

The contractor shall obtain from AQS the state/local-reported PM_{2.5} mass concentrations for these filters, and the full speciation concentration data for filters from the collocated CSN sites and days corresponding to these Teflon filters.

The contractor shall develop a predictive relationship between the light absorption measurement (B_{abs}) and filter elemental carbon loading (and ambient concentration, when integrated flow is included) based on these 48 filters and their corresponding CSN filters and on relevant other data collected by or known to the contractor.

The contractor shall qualitatively and quantitatively assess the degree of agreement between its measurements of mass, elements, elemental carbon, and ions and the measurements originally reported to AQS. The SANDWICH adjusted CSN data, including reduced nitrate estimated to have been collected by the FRM will be used to assist with these comparisons. These data will be provided by EPA (These data are available at http://www.epa.gov/cgi-bin/htmSQL/mxplorer/query_spe.hspl.) The degree of uniformity between XRF elemental analysis, particularly for the components needed to estimate the crustal component (Al, Si, Fe, Ca and Ti), will be compared with collocated CSN measurements. Systematic causes of disagreement shall be investigated, e.g., that filters collected on days when ambient nitrate was absent in fact have nitrate present in the current analysis, that filters collected when nitrate was present appear to have more of a nitrate deficit compared to CSN filters than can be explained by SANDWICH concepts, etc.

Deliverable: A data report on the analyses and on the qualitatively and quantitative assessment of the degree of agreement between the measurements, taking into account SANDWICH concepts and adjustments, with recommendations as to whether the degree of agreement justifies proceeding with Task 4. This may be a memo style report. If the recommendation is to proceed, the report shall also include conclusions regarding the data quality likely to be achieved under Task 4 and caveats that should be included in any EPA dissemination of the data and findings from Task 4. The report shall also include any changes to the original Work Plan for Task 4 needed to increase the success of the project.

Task 4 - Obtain and Analyze 394 State/local Field-Collected Filters, Prepare Memo style Report, and Submit Data to EPA

EPA shall contact the identified state/local monitoring officials to arrange for appropriate packaging and pre-paid shipping of the 394 filters identified in Attachment 1.1 as targets for this Task. Also, the EPA will obtain from these officials the reported PM_{2.5} mass concentration and any associated data that will be needed to complete calculations of concentrations that is not obtainable directly from AQS, such as the integrated filter air flow for the sample. EPA will provide this information to the contractor.

For these 394 field samples, the following filter chemical analyses will be performed: 120 with XRF and IC, 244 with XRF only, and 244 with IC only. Attachment 1.1 identifies which filters will have which chemical analyses. All 394 filters will have light absorption measurements made. The order of multiple analyses will be the same as in Task 2. In general, filters collected on days expected to have high nitrate concentrations have been split about 50/50 between getting only IC and only XRF since if both measurements are made on the same filter the IC results for nitrates will be invalid due to the use of vacuum during the XRF analysis. Filters collected on days expected to have low nitrate will be subject to both XRF and IC analysis.

The contractor shall calculate element and ion ambient concentrations for these filters, using the integrated sample flow obtained from the state/local monitoring officials.

The contractor shall apply the predictive relationship between the light absorption measurement (B_{abs}) and filter elemental carbon loading (and ambient concentration, when integrated flow is included) developed in Task 3 to all 394 filters to generate and estimate elemental ambient carbon concentrations for each.

Using the PM_{2.5} mass, and elemental carbon concentration described above, the contractor will also estimate the organic carbon mass (OCM) by material balance. As described in Frank (2006), this represents an upper bound of OCM.

Deliverables:

A data report on the analyses and the estimates of ambient concentrations (a memo style report is sufficient).

A qualitative report containing any gained insights into data quality and necessary caveats for its use. (a memo style report is sufficient).

The contractor shall submit the B_{abs} measurements and the concentration estimates for PM_{2.5} species for these 394 filters to EPA. EPA will arrange for the submittal of this data to AQS and will create any new method or parameter codes to correctly distinguish estimated concentrations from actually measured concentrations represented by standard AQS method and parameter codes.

Attachment 2.**EQUATION TO ESTIMATE PARTICLE BOUND WATER⁶**(replicates AIM⁷ at FRM equilibration conditions)

First, let $D = \text{NH}_4\text{s} / \text{SO}_4$, $0 < D < 0.375$, where NH_4s is the amount associated with SO_4 .
 i.e. $\text{NH}_4\text{s} = \min(0.375 * \text{SO}_4, \max(0, \text{NH}_4 - 0.29 * \text{NO}_3))$ and where NO_3 is the adjusted NO_3 to represent the amount retained on an FRM filter.
 [The corresponding molar Degree of Neutralization (DON) varies from 0 to 2, i.e. up to 2 moles of NH_4 are needed to fully neutralize the sulfate ion.]

Next, define relative amounts of SO_4 , NO_3 and NH_4 , where measured $\text{NH}_4 \geq 0$ and is capped at a level to fully neutralize NO_3 and SO_4 , i.e., $\text{NH}_4\text{c} = \max((0.375 * \text{SO}_4 + 0.29 * \text{NO}_3), \text{NH}_4)$. Units of SO_4 , NO_3 and NH_4 are $\mu\text{g}/\text{m}^3$.

Finally, define the following normalized parameters:

$$\begin{aligned} S &= \text{SO}_4 / (\text{SO}_4 + \text{NO}_3 + \text{NH}_4\text{c}); \\ N &= \text{NO}_3 / (\text{SO}_4 + \text{NO}_3 + \text{NH}_4\text{c}); \\ \text{and } A &= \text{NH}_4 / (\text{SO}_4 + \text{NO}_3 + \text{NH}_4\text{c}). \end{aligned}$$

Then the amount of particle bound water (WATER) associated with measured SO_4 , adjusted NO_3 and measured NH_4 is calculated according to the estimated degree of neutralization as follows:.

High acidity: DON < 1.2 (D < 0.225)

$$\begin{aligned} \text{WATER} = & [595.556 - 1440.585 * S - 1126.488 * N + 283.907 * (S^{**1.5}) - 13.384 * (N^{**1.5}) \\ & - 1486.711 * (A^{**1.5}) + 764.229 * (S^{**2}) + 1501.999 * (N * S) + 451.873 * (N^{**2}) \\ & - 185.183 * (S^{**2.5}) - 375.984 * (S^{**1.5}) * N - 16.895 * (S^{**3}) - 65.814 * (N^{**1.5}) * S \\ & + 96.825 * (N^{**2.5}) + 83.037 * (N^{**1.5}) * (S^{**1.5}) - 4.419 * (N^{**3}) \\ & + 1720.818 * (A^{**1.5}) * S + 1220.383 * (A^{**1.5}) * N - 311.496 * (A^{**1.5}) * (S^{**1.5}) \\ & + 148.771 * (A^{**1.5}) * (N^{**1.5}) + 1151.648 * (A^{**3})] * (\text{SO}_4 + \text{NO}_3 + \text{NH}_4) \end{aligned}$$

Low acidity: DON > 1.2 (D > 0.225)

$$\begin{aligned} \text{WATER} = & [202048.975 - 391494.647 * S - 390912.147 * N + 442.435 * (S^{**1.5}) - \\ & 155.335 * (N^{**1.5}) - 293406.827 * (A^{**1.5}) + 189277.519 * (S^{**2}) + 377992.610 * N * S \\ & + 188636.790 * N^{**2} - 447.123 * S^{**2.5} - 507.157 * S^{**1.5} * N - 12.794 * S^{**3} \\ & + 146.221 * N^{**1.5} * S + 217.197 * N^{**2.5} + 29.981 * N^{**1.5} * S^{**1.5} - 18.649 * N^{**3} + \\ & 216266.951 * A^{**1.5} * S + 215419.876 * A^{**1.5} * N - 621.843 * A^{**1.5} * S^{**1.5} \\ & + 239.132 * A^{**1.5} * N^{**1.5} + 95413.122 * A^{**3}] * (\text{SO}_4 + \text{NO}_3 + \text{NH}_4) \end{aligned}$$

The above equations performs well with three decimal places (error < 3%). With two decimal places, error is -3 to +10 %. With one decimal, the low acidity equation has very high positive error.

Regarding the notation for the above equations, * denotes multiplication and ** denotes exponentiation.

⁶ This equation, developed by N. Frank is included in EPA *Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM_{2.5}, and Regional Haze* <http://www.epa.gov/scram001/guidance/guide/final-03-pm-rh-guidance.pdf>

⁷ Clegg, S.L.; Brimblecombe, P.; Wexler, A.S. Thermodynamic Model of the System $\text{H}_2\text{O}-\text{NH}_3-\text{SO}_2-\text{NO}_3-\text{H}_2\text{O}$ at Tropospheric Temperatures; *J. Phys. Chem.* **1998**, *102*, 2137-2154.